Post-Collision-Interaction Effects in HCl Following Photofragmentation Near the Chlorine K-Edge

D. L. Hansen, G. B. Armen,[1] M. E. Arrasate, J. Cotter,[2] G. R. Fisher,[3] K. T. Leung,[4]
J. C. Levin,[1] R. Martin, P. Neill,[2] R. C. C. Perera,[3] I. A. Sellin,[1]
M. Simon,[5,6] Y. Uehara,[7] B. Vanderford, S. B. Whitfield,[8] and D. W. Lindle
Department of Chemistry, University of Nevada, Las Vegas, NV 89154-4003
[1] *Department of Physics, University of Tennessee, Knoxville, TN 37996*
[2] *Department of Physics, University of Nevada, Reno, NV 89557-0058*
[3] *Lawrence Berkeley National Laboratory, Berkeley, CA 94720*
[4] *Department of Chemistry, University of Waterloo, Canada, N2L 3G1*
[5] *LURE, Bâtiment 209D, Université Paris-Sud, 91405 Orsay Cedex, France*
[6] *CEA/DRECAM/SPAM, Bâtiment 522, CEN Saclay, 91191 Gif/Yvette Cedex, France*
[7] *Mitsubishi Electric Corporation, Amagasaki, Hyogo, 661 Japan*
[8] *Department of Physics and Astronomy, University of Wisconsin, Eau Claire, WI 54702*

Ion time-of-flight mass spectroscopy was used to study the relaxation dynamics of HCl following photoexcitation in the vicinity of the Cl K threshold (≈2.8 keV) using light from B.L. 9.3.1 at the ALS. We present the first detailed quantitative analysis describing PCI-moderated dissociation of molecules. We find that recapture effects observed in the ion yields of Cl^{n+} following photodissociation of HCl are related to K-shell-Auger emission, and that these effects in molecules can be described with a hydrogenic PCI model. In addition, we also find that the H^+ yield increases in the first few eV immediately above threshold, suggesting that this fragment sometimes captures the Cl 1s photoelectron, an effect which cannot be described using conventional atomic-PCI models.

In the region just above the K-shell threshold at 2829.8 eV, each Cl^{n+} PIY is affected by two PCI-induced electron-recapture effects; a decrease resulting from the loss of Cl^{n+} ions to the $Cl^{(n-1)+}$ charge state, and an increase arising from $Cl^{(n+1)+}$ ions recapturing electrons to become Cl^{n+}. For example, the yield of Cl^{4+} will be reduced by Cl^{4+} ions which recapture electrons and become Cl^{3+}, but will be augmented by Cl^{5+} ions which recapture and become Cl^{4+}. In order to isolate the recapture effect on each charge state, we first assume that because the Cl^{6+} yield is negligible, PCI trends in the Cl^{5+} PIY (Fig. 1(a)) reflect only the loss of Cl^{5+} ions through electron recapture. Thus, an estimate of the Cl^{5+} relative recapture cross section at energies just above threshold is obtained from the Cl^{5+} PIY by subtracting the near-threshold PIY values from the asymptotic Cl^{5+} yield. The asymptotic yield was taken as the average of the data points around 7 eV, above the energy regime where PCI effects are most prevalent, while below the energy where double-ionization effects begin. This recapture cross section for Cl^{5+} is then subtracted from the Cl^{4+} PIY to give an adjusted PIY curve with the contribution of Cl^{5+} recapture removed (Fig. 1(b) circles). The procedure is then repeated using each adjusted PIY curve, in turn, to isolate the recapture effect on each Cl^{n+} charge state.

In order to interpret the results in Fig. 1, we have attempted to reproduce the modified PIY curves using electron escape probabilities calculated with a hydrogenic model using a core-hole width of 0.6 eV. The hydrogenic model is based on the assumption that once a K-shell hole localized around the Cl atom is created, the intermediate states are localized far from the molecule (i.e. $\langle r \rangle \geq 50$ a.u.). Thus the structure of the core is unimportant, and the electron in the excited state sees an HCl^+ ion. The escape probabilities plotted in Fig. 1 were normalized to the PIY curves above threshold. Within the experimental uncertainties for Cl^{3+}, Cl^{4+}, and Cl^{5+} charge states, the data agree with the K-shell PCI curves indicating that PCI recapture occurs in conjunction with K-shell Auger decay, and that the process of PCI recapture for the Cl^{n+} ions in HCl is similar to that observed in ions formed following

relaxation of excited atomic species. The disagreement between the model and the data for the first two eV above threshold is at least partially explained by the excitation of the Cl K electron to Rydberg orbitals, and the photon and natural line widths.

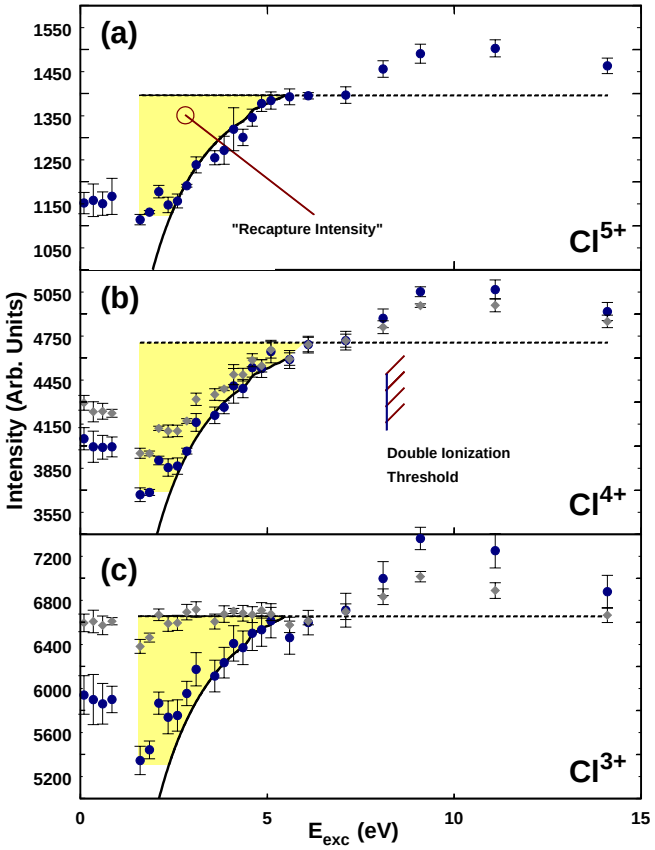

FIG. 1. (a) Partial ion yield (circles) for Cl^{5+}. (b) Partial ion yield (diamonds), and partial ion yield modified for PCI recapture (circles) for Cl^{4+}. (c) Partial ion yield (diamonds), and partial ion yield modified for PCI recapture (circles) for Cl^{3+}. The solid line represents the hydrogenic model for PCI following K-shell Auger electron ejection. No modifications were made to the Cl^{5+} yield because the Cl^{6+} yield was negligible. The dashed line represents the asymptotic limit for single electron ionization. The shaded region represents the loss in intensity as a result of PCI recapture.

Fig. 2 shows the PIY for H^+ (circles) following K-shell photoexcitation, and the TIY (diamonds) normalized to the H^+ PIY. The yield for H^+ increases with energy just above threshold similar to, but smaller than, those observed for the Cl^{n+} ($n \geq 3$) charge states. Comparison to the TIY for HCl indicates that this is not merely a result of a change in cross-section for K-shell excitation of the HCl molecule. Because of the atomic-like PCI behavior for the Cl^{n+} ions it seems that a likely explanation for the data is recapture of the photoelectron by H^+ following dissociation of the molecule, suggesting that the H^+ fragment also is involved in PCI, occasionally recapturing the Cl 1s photoelectron. This marks the first observation of PCI-mediated fragmentation, where the photoelectron is recaptured by an ion around which the initially excited orbital is not localized.

Comparison of the H^+ yield to the hydrogenic model, as well as to a semi-classical model for PCI shows a clear deviation of the data from PCI theory. This is hardly surprising because the empirical formula is based on the assumption that the electrons are receeding in a spherical Coulombic potential. This is not the situation at the time of Auger decay due to

perturbations in the potential well resulting from the close proximity of the H^+ ion, and the fact that recapture by H^+ is a molecular effect, and is not included in the current models; an entirely new physical effect is being observed.

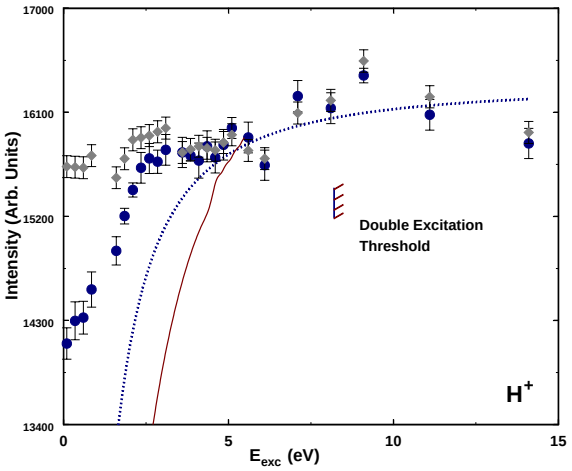

FIG. 2. Partial ion yield for hydrogen (circles), and total ion yield for HCl (diamonds). The TIY has been normalized to the H^+ PIY in order to facilitate comparison. The solid line represents the hydrogenic model for PCI following K-shell Auger electron ejection, the dotted line represents the semi-classical model.

The possibility that the photoelectron is recaptured while the hydrogen atom is still part of the molecule is worthy of mention. The H^+ PIY shows the greatest deviation from the TIY in the first 2.5 eV above resonance. We previously noted that the PIYs for the Cl^{n+} ions did not follow the PCI curves in this energy regime and attributed it to excitations to Rydberg orbitals, coupled with photon and natural line widths. In most cases, if the photoelectron is recaptured in a molecular orbital, the molecule will still dissociate, and because of its higher electronegativity, the Cl^{n+} ion would most likely retain the electron instead of the hydrogen. This process produces an identical result to the case where recapture by $Cl^{(n+1)+}$ follows fragmentation. An exception to this may arise if the electron is recaptured in an anti-bonding orbital, leading sometimes to neutral dissociation, as observed previously following resonant excitation to the $6\sigma^*$ orbital. In addition, in cases where the photoelectron is ejected in the direction of the H^+ ion, it is possible for recapture by H^+ to occur whether or not an Auger electron is emitted. Regardless of the explanation(s) for the PCI effect on the H^+ PIY, it is clear that a novel physical effect, unexplainable by conventional models of PCI, has been observed.

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Team Leader: Dennis Lindle, E-mail: lindle@nevada.edu, Fax: 1 702 895 4072